

THE EFFECTS OF DIFFUSION ON OXYGEN ISOTOPES IN EARTH'S UPPER ATMOSPHERE. M. Brin-jiki¹, and J. R. Lyons², ¹Arizona State University, School of Earth and Space Exploration, mbrinjik@asu.edu, ²Arizona State University, School of Earth and Space Exploration, jrylons2@asu.edu

Introduction: Many science missions are exploring the atmospheres of planetary bodies in the Solar System. One of the main goals of the Mars Atmosphere and Volatile Evolution (MAVEN) spacecraft is understanding how the Martian atmosphere evolved over time; this is accomplished in part by measuring the loss rates of various gases and determining the ratio of stable isotopes in the upper Martian atmosphere [1]. To place the results from MAVEN and the atmosphere of Mars, in general, in a larger solar system context, we need to study similar processes in the upper Earth atmosphere. To this end, we are working to better understand the stable oxygen isotope abundances and the processes that affect them in Earth's thermosphere, specifically isotope fractionation due to mass-independent processes such as photodissociation. The main goal of this work is to model Earth's upper atmosphere in terms of the number densities and delta values of ¹⁶O, ¹⁷O, and ¹⁸O: first, using simple equations from atmospheric diffusion theory, and then using the more sophisticated VULCAN photochemical code.

Atmospheric Structure. The thermosphere of the Earth begins at the homopause, which is about 100 kilometers above the surface. The homopause defines the transition between an atmosphere mixed by eddy diffusion (below) and molecular diffusion (above). Above the homopause, heavier species have smaller scale heights than lighter species due to diffusive separation. Isotope fractionation refers to various processes that change the relative abundances of isotopes. Mass-dependent fractionation processes (MDF) are when the abundance of isotope scales with the mass of each isotope. Mass-independent fractionation (MIF) is when the abundance of the isotopes scales by some other process. We expect that below the homopause there is very little fractionation of isotopes due to eddy diffusion, while above the homopause diffusive separation results in stronger mass-dependent fractionation.

To quantitatively describe the effects of isotope fractionation, geochemical 'delta' notation is used. Values are given in per mill (‰). For oxygen, the ratio of two stable isotopes relative to a standard is given by $\delta^x O = 10^3 (R_{sample}^x / R_{standard}^x - 1)$ where $R^x = {}^x O / {}^{16} O$ for $x = 17$ or 18 . We can compute the quantity $\Delta^{17} O = \delta^{17} O - 0.528 \delta^{18} O$ which describes deviation from mass-dependent processes. Materials in the atmosphere should have $\Delta^{17} O = 0$.

Methods:

Diffusion Theory Model. Atomic oxygen becomes an important constituent in the atmosphere above the homopause [2]. Oxygen isotope abundances have been studied for many years but not at altitudes above the homopause. From theory [2], the molecular diffusion coefficient (in $\text{cm}^2 \text{s}^{-1}$) for the different oxygen isotope species can be approximated as:

$$D_{12} = 1.96 \cdot 10^6 (1/m_1 + 1/m_2)^{1/2} (T^{1/2}/n)$$

where m_1 and m_2 are the mass of the background air and the mass of the isotope in grams, n is the number density of the background atmosphere approximated as $n = n_i e^{-z/H}$, and H is the scale height of the background atmosphere below the homopause: $H = \frac{kT}{mg}$.

Due to diffusive separation, the scale height of each oxygen isotope will be slightly different than the scale height of the air below the homopause: $H_i = \frac{kT}{m_i g}$.

These components are required for the number density equation:

$$n_x(z) = n_{i,x} \cdot \exp \left[\int_{z_0}^z \left(\frac{1}{H_i} + \frac{1}{H} \frac{K}{D_{12}} \right) \left(1 + \frac{K}{D_{12}} \right)^{-1} dz \right]$$

where $n_{i,x}$ is the number density at the bottom of the atmosphere for isotope x , and K is the eddy diffusion coefficient. For this model, we approximate the atmosphere as isothermal with a temperature of 500 K, and the eddy diffusion coefficient as constant with a value of $10^5 \text{ cm}^2 \text{ s}^{-1}$. For altitudes up to 500 km, we calculated the number densities for ¹⁶O, ¹⁷O, and ¹⁸O.

VULCAN. We then employed VULCAN, a photochemical kinematics code, for a more accurate look at the number densities of oxygen isotopes in the upper Earth atmosphere. VULCAN utilizes a realistic temperature profile for Earth and includes chemistry and photochemistry for the most important chemical species in the atmosphere [3]. However, it does not include isotopes or ion chemistry, so we modified the code to include oxygen isotopes. The number densities from VULCAN are shown in Figure 1 with the results from the isothermal diffusion theory calculation.

Results: Figure 1 shows the number densities for the stable oxygen isotopes calculated using diffusion theory and VULCAN. The solid lines are the results from the diffusion theory equations, and the dashed lines are the VULCAN results. The number density (in cm^{-3}) for ¹⁶O is in blue, ¹⁷O is in green, and ¹⁸O is in red.

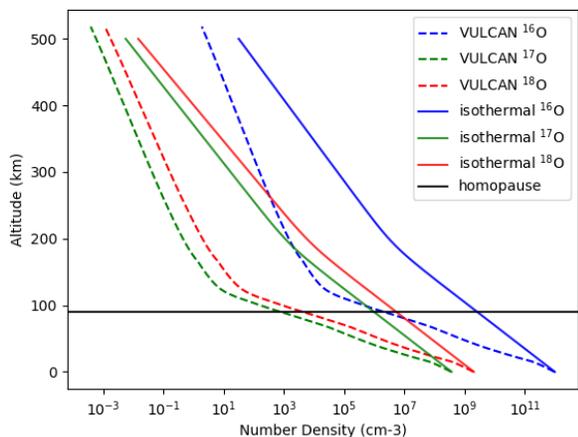


Figure 1. The number densities for the stable oxygen isotopes, calculated from diffusion theory (solid lines) and using VULCAN (dashed lines). The homopause is shown with the solid black line.

We expect to see the slope of the number density lines to be different below and above the homopause (due to diffusive separation). The diffusion theory approximation has a slope change at around 200 km due to the assumed isothermal temperature profile. The VULCAN results diffusively separate closer to 100 km, the true Earth homopause.

Delta values. Figure 2 shows the values for $\delta^{17}O$ and $\delta^{18}O$ (‰) calculated using diffusion theory (solid lines) and VULCAN (dashed lines).

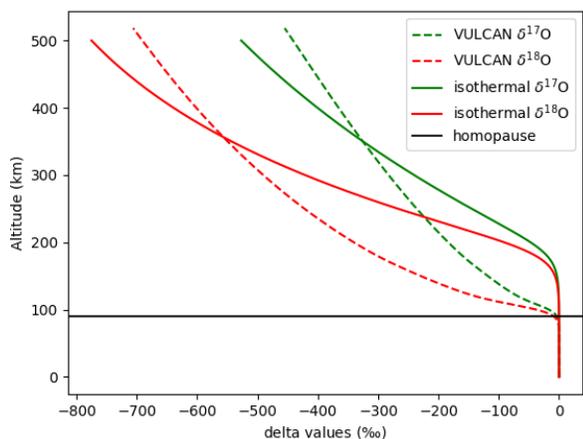


Figure 2. The delta values (‰) for $\delta^{17}O$ and $\delta^{18}O$ calculated from diffusion theory (solid lines) and using VULCAN (dashed lines). The homopause is shown with the solid black line.

The delta values from the diffusion theory approximation are depleted by about 100 ‰ more than the VULCAN results for both $\delta^{17}O$ and $\delta^{18}O$.

$\Delta^{17}O$ plots. Figures 3 and 4 show $\Delta^{17}O$ from diffusion theory (solid lines) and VULCAN (dashed lines). However, the slope factor of 0.528 results in $\Delta^{17}O$ enrichments on the order of 40 ‰, shown in Figure 3.

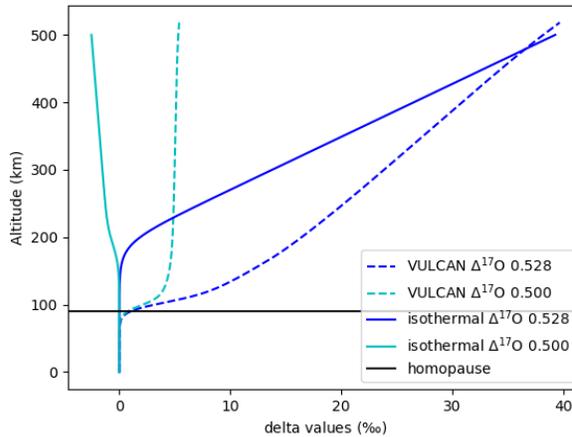


Figure 3. The $\Delta^{17}O$ values (‰) calculated from diffusion theory (solid lines) and using VULCAN (dashed lines).

Based on the barometric law behavior of the individual isotopes undergoing molecular diffusion, we redefined $\Delta^{17}O = \delta^{17}O - 0.500\delta^{18}O$ which results in a $\Delta^{17}O$ depletion of -2 ‰ from the diffusion theory calculation and an enrichment of 5 ‰ from VULCAN, shown in Figure 4.

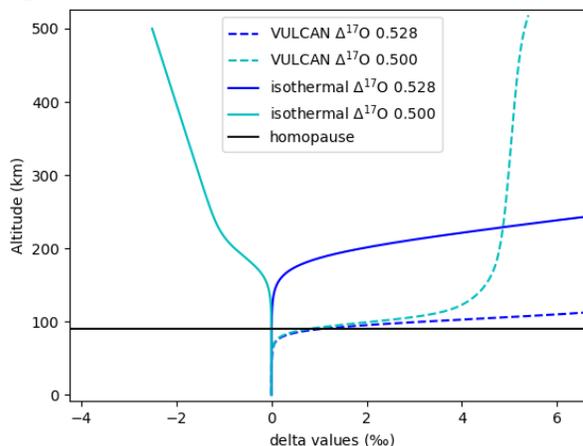


Figure 4. The $\Delta^{17}O$ values (‰) calculated from diffusion theory (solid lines) and using VULCAN (dashed lines), zoomed in to show the relevant values.

Conclusions: We find that diffusion of isotopes in the upper atmosphere follows mass-dependent behavior, but with a 0.500 factor in the fractionation law rather than 0.528. This is a result of barometric law behavior rather than the usual mass-dependence of isotopic zero-point energies. Use of the 0.528 factor yields large and false anomalous isotope behavior.

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References: [1] B.M. Jakosky et al. (1994) *Icarus*, 111, 2, 271-288. [2] P.M. Banks and G. Kockarts. (1973) *Aeronomy, Chapter 15*. 32-63. [3] S.M. Tsai et al. (2017) *ApJS*, 228, 2.